

# PATENT SPECIFICATION

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## (54) PREPARATION OF CARBOXYLIC ESTERS AND/OR ACIDS

(71) We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V., a company organized under the laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the preparation of carboxylic acids and/or carboxylic esters having the general formula  $R^1-CO-O-R^2$ , wherein  $R^1$  and  $R^2$  represent organic radicals which may be the same or different from each other.

It is known to convert aliphatic ethers into carboxylic esters by reacting an aliphatic ether with carbon monoxide using a liquid mixture of boron trifluoride, orthophosphoric acid and water as a catalyst. This known process is carried out at a relatively high pressure and temperature, that is to say preferably at a pressure of about 350—700 atmospheres and at a temperature between 150° and 400°C. The aliphatic ether should be present in the gaseous state.

It is an object of the present invention to provide a process in which an ether is reacted with carbon monoxide at a relatively low pressure and temperature, a very high ether conversion nevertheless being obtained.

This object is achieved by using a catalyst of very special composition.

The invention, accordingly, provides a process for the preparation of a carboxylic acid and/or carboxylic ester having the general formula  $R^1-CO-O-R^2$ , wherein  $R^1$  and  $R^2$  represent organic radicals which may be the same or different from each other, by reacting an ether of the formula  $R^1-O-R^2$  with carbon monoxide in the presence of an acid catalyst, in which process a liquid catalytic mixture is used of boron trifluoride, orthophosphoric acid and a compound of the general formula  $R^3OH$ , wherein  $R^3$  represents a hydrogen atom or an organic radical, boron trifluoride and the

compound  $R^3OH$  being used in a molar ratio in the range of from 1:1 to 1:2.3.

When a catalyst having a composition within the special range according to the process of the invention is used, the ether is often substantially completely converted, carboxylic esters mainly being formed. By-products may include carboxylic acids. This surprisingly high activity is not found when a catalyst composition outside the said special range is applied. It is preferred that boron trifluoride and the compound  $R^3OH$  are used in a molar ratio in the range of from 1:1 to 1:2, since in this range the catalytic activity is optimal. Most preferred are molar ratios in the range of from 1:1.2 to 1:2.

Phosphoric acid should be present in the catalyst as it prevents, or at all events restricts, decomposition of boron trifluoride, which decomposition otherwise may become quite appreciable at temperatures above 60°C. If boron trifluoride and orthophosphoric acid are used in a molar ratio of for example 1.6:1 or even 1:1, so that the catalyst has a relatively high phosphoric acid content, this may give rise to excessive corrosion of various parts of the equipment used. It has now been found that when boron trifluoride and orthophosphoric acid are used in a molar ratio  $BF_3/H_3PO_4$  in the range of from 2:1 to 20:1, the corrosion rate may be suppressed. More preferred are molar ratios  $BF_3/H_3PO_4$  between 2:1 and 10:1, and in particular between 2.5:1 and 10:1. Still more preferred are molar ratios between 2.5:1 and 4.5:1. Molar ratios  $BF_3/H_3PO_4$  between 3:1 and 4.5:1 are often optimal, giving high yields of esters.

The abovementioned molar ratios refer to the overall composition only and are independent of any form in which the three components might be present in the catalytic mixture.

An attractive feature of the process according to the present invention is that it may be carried out at relatively low tem-

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perature, preferably in the range of from 50°C to 150°C. Such a low temperature range is favourable for counteracting undesired side reactions and corrosion. Reaction temperatures in the range of from 60°C to 120°C are particularly preferred.

The carbon monoxide pressure during the process according to the invention can be varied between wide limits. It is to be considered as an advantage presented by the process according to the invention that it gives satisfactory results already at fairly low pressures, in particular below 250 kg/cm<sup>2</sup> abs., preferably in the range of from 30 to 150 kg/cm<sup>2</sup> abs. The lower limit of the said partial pressure may be for example 10 kg/cm<sup>2</sup> abs.

The carbon monoxide used in the process of the invention may originate from any suitable source. It is admissible to use a gas which is a mixture of carbon monoxide with one or more inert gases, including, for example, hydrogen, nitrogen or gaseous alkanes. However, the carbon monoxide concentration in such a gas is preferably at least 50% by volume, and the use of pure or substantially pure carbon monoxide is most preferred. If desired, precursors of carbon monoxide, for example formic acid, may be used. If gaseous mixtures of carbon monoxide are used, the above pressures are to be related to the carbon monoxide partial pressures in the mixtures.

The process according to the invention allows use of the ether in the liquid state. This, of course, presents advantages with respect to the size of the equipment in which the reaction is performed, compared with processes in which the ether is in the gaseous state.

The volume ratio between the liquid catalytic mixture and the ether (in batch or continuous operation) may vary between wide limits, but the range of from 6:1 to 0.5:1 is usually to be preferred, the range of from 4:1 to 1:1 being most preferred.

The ester yield is favourably influenced by stirring vigorously. Therefore, the reaction is preferably carried out in a reactor provided with a stirrer having a power input of at least 0.5 hp per m<sup>3</sup> and in particular between 1 and 4 hp per m<sup>3</sup> liquid reactor contents. Mixing is further improved when the reaction is carried out in a reactor provided with one or more baffles. Very good mixing is obtained with a stirred reactor provided with four baffles.

The process according to the invention can be carried out batchwise, semi-continuously or continuously. For each of these embodiments any suitable known technique and apparatus may be used. In batchwise operation the liquid catalytic mixture is for instance introduced into an autoclave, carbon monoxide is added to a pressure of say

100 kg/cm<sup>2</sup> abs., and an ether is pumped into the autoclave with stirring or shaking. After some time the reaction liquid is withdrawn and one or more carboxylic esters are isolated from this liquid.

An attractive continuous procedure is one according to which the compounds to be reacted and the liquid catalytic mixture are added continuously to a reaction mixture, the composition of which remains substantially constant, which is kept substantially homogeneous by stirring, and which is also continuously withdrawn. Also, the reaction mixture can be passed through several of such reactors placed in series, which permits choosing the most appropriate conditions of pressure, temperature and composition in each reaction vessel. The carbon monoxide may be introduced directly into the liquid or it may be led into a gaseous phase present above the reaction mixture or it may be introduced in both ways at the same time. It may be introduced on one place into the reactor or at several places simultaneously.

At the end of the reaction the carboxylic ester(s) formed may be isolated from the reaction mixture in any suitable manner. The mixture may, for example, be extracted by means of a suitable solvent and the esters may be isolated from the extract obtained by conventional means, for example by distillation. The liquid catalytic mixture which is obtained as the raffinate in this extraction, is preferably reused. If desired part of this catalyst liquid may be discarded and replenished by fresh catalyst liquid.

The liquid catalytic mixture may be made in a simple manner by adding orthophosphoric acid, boron trifluoride and the compound R<sup>3</sup>OH to each other.

The present process may be used for the conversion of a great variety of ethers into carboxylic esters and/or carboxylic acids. An ether in which R<sup>1</sup> and R<sup>2</sup> are identical is converted into an ester of the general formula R<sup>1</sup>COOR<sup>2</sup>, wherein the R<sup>1</sup> and R<sup>2</sup> represent the same organic radical. For example, dimethyl ether is converted into methyl acetate.

An ether in which R<sup>1</sup> and R<sup>2</sup> are not identical is usually converted into a mixture of esters having the general formula R<sup>1</sup>COOR<sup>2</sup> and R<sup>2</sup>COOR<sup>1</sup>. The ratio of the respective esters formed will depend on the ratio between the rate at which the ether is cleft between the R<sup>1</sup> group and the oxygen atom and the rate at which it is cleft between the R<sup>2</sup> group and the oxygen atom.

Suitable organic radicals represented by R<sup>1</sup> and R<sup>2</sup> consist of aliphatic radicals, cycloaliphatic radicals, aralkyl radicals, and aryl radicals, such as for example methyl, n-butyl, isopropyl, tertiary pentyl, cyclo-

hexyl, cycloheptyl, benzyl, tolyl, xylyl, phenyl and naphthyl radicals.

Ethers in which the said  $R^1$  and  $R^2$  represent the same or different hydrocarbon radicals having from 1 to 10 carbon atoms per radical are quite suitable. Particularly when the radicals are aliphatic, high yields of esters are obtained. Ethers wherein one of the symbols  $R^1$  and  $R^2$  represents a primary alkyl radical having of from 1 to 10 carbon atoms, particularly a methyl or an ethyl group, while the other represents a tertiary alkyl radical having of from 4 to 10 carbon atoms are preferred. Particularly with methyl tertiary butyl ether very high ester yields have been obtained.

Carbonium ions are probably formed as intermediates in this process according to the invention. Such carbonium ions may isomerize, particularly those formed from primary alkyl groups, so that esters are formed therefrom having molecular structures which do not exactly correspond to those of the starting materials. Thus ethers having two primary alkyl groups are converted into a mixture of two esters, for example methyl n-butyl ether is converted into n-butyl acetate and methyl i-valerate, and n-propyl n-butyl ether is converted into n-butyl i-butyrate and n-propyl i-valerate.

Ethers having one primary and one secondary radical are converted predominantly into esters of the general formula  $R^1COOR^2$  wherein  $R^2$  represents the primary and  $R^1$  the secondary radical, for example n-propyl isopropyl ether is mainly converted into n-propyl isobutyrate.

Ethers having one primary and one tertiary radical are as a rule substantially completely converted into an ester of the general formula  $R^1COOR^2$ , in which  $R^2$  represents the primary and  $R^1$  the tertiary radical. For example, methyl tertiary-butyl ether is substantially completely converted into the methyl ester of trimethylacetic acid, and methyl tertiary-pentyl ether into the methyl ester of  $\alpha,\alpha$ -dimethylbutanoic acid, no by-products being formed.

From alkyl aryl ethers the alkyl group is usually initially split off and an ester is formed of the general formula  $R^1COOR^2$ , in which  $R^1$  represents the alkyl and  $R^2$  the aryl group. Methyl phenyl ether, for example, is predominantly converted into phenyl acetate, and t-butyl phenyl ether into the phenyl ester of trimethyl acetic acid.

Alkyl aralkyl ethers are predominantly converted into esters of the general formula  $R^1COOR^2$ , in which  $R^1$  represents an aralkyl group and  $R^2$  an alkyl group. For example, methyl benzyl ether is mainly converted into methyl phenylacetate.

When  $R^1$  is a secondary or a tertiary alkyl

radical, and  $R^2$  is a primary, or a secondary or tertiary, alkyl radical, respectively,  $R^3OH$  preferably represents an alcohol wherein  $R^3$  is identical with  $R^2$ . For example, if methyl tertiary-butyl ether is to be converted into methyl pivalate, methyl alcohol is preferably used as the compound  $R^3OH$ . The reason for this is that the compound  $R^3OH$  is not entirely unaffected by the reaction process, esters of the formula  $R^2COOR^3$  or  $R^1COOR^3$  as well as alcohols of the general formula  $R^1OH$  or  $R^2OH$  generally being formed as by-products. In continuous operation the by-product alcohols  $R^1OH$  and  $R^2OH$  will gradually replace  $R^3OH$  in the catalyst. Accordingly, if  $R^3$  is not identical with  $R^1$  or  $R^2$  in the long run only esters of the formula  $R^2COOR^1$  or  $R^1COOR^2$  will be produced, anyway. However, it is preferable to avoid the complications arising in the beginning when  $R^3$  is not  $R^1$  or  $R^2$ .

When it is preferred to produce a mixture of carboxylic acids and esters, the compound  $R^3OH$  is preferably water. The by-products of the reaction will then be carboxylic acids of the formula  $R^2COOH$  and  $R^1COOH$ . The by-products may be separated from the esters by conventional techniques, such as fractional distillation.

The esters prepared according to the invention may, for example be applied as solvents. Methyl pivalate, for example, is a stable solvent. It may be used for the selective extraction of metals from aqueous solutions of their salts, for example of iron (III) from solutions containing iron (III) and, for instance, copper (II), cobalt (II) and/or nickel (II).

The process of the invention is further elucidated by way of the following Example.

#### EXAMPLE

A vessel made of "Hastelloy C", having a volume of 1 litre provided with a mechanical stirrer and four baffles was charged with 250 ml (415 grams) of a liquid  $H_3PO_4/BF_3/H_2O$  catalyst of a molar composition 1:4:6.5. The temperature of the vessel was kept at 100°C and pure carbon monoxide was used to maintain a total pressure of 100 kg/cm<sup>2</sup> in the vessel at 100°C. The stirrer speed was 800 revolutions per minute. 194 g of methyl tertiary-butyl ether were continuously supplied to the vessel for 90 minutes. Then, the vessel was depressurized and the reaction mixture four times extracted with an equal volume of n-pentane. The four extracts were combined, the n-pentane was distilled off and the residue obtained was analysed with the aid of gas chromatography. The composition of the residue was as follows:

|   | %m   |
|---|------|
| Methyl pivalate ... ..                        | 52.0 |
| pivalic acid ... ..                           | 31.0 |
| methyl ester higher than methyl pivalate      | 11.5 |
| 5 C <sub>6</sub> -C <sub>8</sub> acids ... .. | 1.0  |
| C <sub>9</sub> — acids ... ..                 | 3.5  |
| compounds other than esters and acids         | 1.0  |

#### WHAT WE CLAIM IS:—

1. A process for the preparation of a  
10 carboxylic acid and/or carboxylic ester  
having the general formula  $R^1-CO-O-R^2$   
wherein  $R^1$  and  $R^2$  represent organic radicals  
which may be the same or different from  
each other, by reacting an ether of the  
15 formula  $R^1-O-R^2$  with carbon monoxide  
in the presence of an acid catalyst, in which  
process a liquid catalytic mixture is used  
of boron trifluoride, orthophosphoric acid  
and a compound of the general formula  
20  $R^3OH$ , wherein  $R^3$  represents a hydrogen  
atom or an organic radical, boron tri-  
fluoride and the compound  $R^3OH$  being  
used in a molar ratio in the range of from  
1:1 to 1:2.3.

2. A process as claimed in claim 1, in  
25 which the said ratio has a value in the range  
of from 1:1.2 to 1:2.

3. A process as claimed in claim 1 or 2,  
30 in which boron trifluoride and orthophos-  
phoric acid are used in a molar ratio  
( $BF_3/H_3PO_4$ ) in the range of from 2:1 to  
20:1.

4. A process as claimed in claim 3, in  
35 which the molar ratio ( $BF_3/H_3PO_4$ ) has a  
value in the range of from 2.5:1 to 10:1.

5. A process as claimed in claim 3 or 4,  
in which the molar ratio ( $BF_3/H_3PO_4$ ) has  
a value in the range of from 3:1 to 4.5:1.

6. A process as claimed in any one of  
40 the preceding claims, in which the reaction  
is carried out at a temperature in the range  
of from 50° to 150°C.

7. A process as claimed in claim 6, in  
45 which the reaction is carried out at a tem-  
perature in the range of from 60° to 120°C.

8. A process as claimed in any one of  
the preceding claims, in which a carbon  
monoxide pressure between 10 and 250  
kg/cm<sup>2</sup> abs. is applied.

9. A process as claimed in claim 8, in  
50 which a carbon monoxide pressure in the  
range of from 30 to 150 kg/cm<sup>2</sup> abs. is  
applied.

10. A process as claimed in any one of  
55 the preceding claims, in which a volume  
ratio between the liquid catalytic mixture  
and the ether in the range of from 6:1 to  
0.5:1 is applied.

11. A process as claimed in claim 10,  
60 in which a volume ratio between the liquid

catalytic mixture and the ether in the range  
of from 4:1 to 1:1 is applied.

12. A process as claimed in any one of  
the preceding claims, in which the reaction  
is carried out in a reactor provided with a  
65 stirrer having a power input of at least 0.5  
hp per m<sup>3</sup> liquid reactor contents.

13. A process as claimed in claim 12,  
in which the reactor used is provided with  
one or more baffles. 70

14. A process as claimed in any one of  
the preceding claims, in which an ether of  
the said formula is used in which  $R^1$  and  $R^2$   
represent the same or different hydrocarbon  
radicals having from 1 to 10 carbon atoms  
75 per radical.

15. A process as claimed in claim 14,  
in which the said hydrocarbon radicals are  
aliphatic radicals.

16. A process as claimed in claim 15,  
80 in which one of the symbols  $R^1$  and  $R^2$   
represents a primary alkyl radical having  
from 1 to 10 carbon atoms, while the other  
represents a tertiary alkyl radical having  
of from 4 to 10 carbon atoms. 85

17. A process as claimed in claim 16,  
in which the ether used is a methyl or an  
ethyl ether.

18. A process as claimed in claim 17,  
90 in which the ether used is methyl tertiary-  
butyl ether.

19. A process as claimed in any one of  
the preceding claims in which in the com-  
pound  $R^3OH$  used  $R^3$  is identical with  $R^1$   
or  $R^2$ . 95

20. A process as claimed in claim 19,  
in which  $R^1$  is a secondary or a tertiary  
alkyl radical, and  $R^2$  is a primary, or a  
secondary or tertiary, alkyl radical, respec-  
tively, while  $R^3OH$  represents an alcohol  
100 wherein  $R^3$  is identical with  $R^2$ .

21. A process as claimed in claim 20,  
in which for the conversion of methyl ter-  
tiary-butyl ether into methyl pivalate the  
compound  $R^3OH$  is methyl alcohol. 105

22. A process as claimed in any one of  
claims 1 to 18, in which the compound  
 $R^3OH$  is water.

23. A process as claimed in claim 1 and  
substantially as hereinbefore described. 110

24. A process for the preparation of a  
pivalic acid ester substantially as herein-  
before described with reference to the Ex-  
ample.

25. Carboxylic acids and/or esters of  
115 carboxylic acids prepared by the process  
claimed in any one of the preceding claims.

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